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Canada

Kinetics of Arsenic and Nickel in Sediments in Moira Lake

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MICROMEDIA

SUMMARY

Ni and As behaviour in surface waters located downstream of U tailings will be incorporated into environmental assessments of several tailings sites. Historical discharges of Ni and As from tailings into Moira Lake provided the opportunity to measure the distribution and fluxes of both elements in this contaminated environment. In this report the diffusive and particulate fluxes of Ni and As from water to bottom sediments were calculated from Pb-210 dating and measured element concentrations or porewater gradients. Ni and As diffused simultaneously both from the sediments across the interface into the overlying water and deeper into the sediments. Diffusion rates were greater than bulk accumulation rates of Ni and As and cannot be ignored in models of contaminant movement through freshwaters. Moira Lake provides a useful system where assessment models can be tested and calibrated to improve model predictions.

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1. INTRODUCTION

1.1 RATIONALE

In some uranium ore deposits in Saskatchewan, arsenic and nickel comprise up to two percent of the tailings by weight (Beak 1986). Both elements may be toxic to biota and discharged from the tailings into groundwaters and surface waters. Since a major objective of the National Uranium Tailings Program (NUTP) is developing a mathematical model for assessing the potential environmental hazards present in the tailings, the behaviour and effects of nickel and arsenic must be taken into account.

Information on the geochemistry of Ni and As is needed to predict their future behaviour in surface waters located downstream from the tailings. This study utilizes sediments from Moira Lake which received arsenic and nickel discharge from tailings operations during the past 100 years. As a result of the discharges, the lake sediments contain elevated concentrations of several metals including arsenic and nickel (Mudroch and Capobianco 1980; Evans et al. 1984; Cornett and Chant 1986). Concentrations of contaminants measured in the sediments were more than 1,000 times greater than those measured in the overlying waters (Cornett and Chant 1986). Significant gradients in arsenic and nickel concentration in the sediment porewaters suggest that these elements are mobile in the sediment column. Relatively large concentrations of both nickel and arsenic were bound to the iron and manganese oxides in the sediment, or to carbonates and other easily exchangeable compounds (Cornett and Chant 1986). These observations suggest a significant potential for the transport of contaminants from the sediments into the overlying lake water. The objective of this study is to determine the rates of Ni and As transport between the water and sediments.

1.2 STUDY OBJECTIVES

Arsenic and nickel fluxes across the sediment water interface are driven by two processes: a) the accumulation of particle bound contaminant sorbed onto settling particles, and b) diffusion of contaminants along concentration gradients across the mud-water interface.

The objectives of this study were to:

a) Measure the concentrations of Pb-210 in two sediment cores from Moira Lake.

b) Calculate the bulk dry sediment accumulation rates in the sediment cores using Pb-210 dating.

c) Calculate the rates of Ni and As accumulation in the bottom sediments using the Pb-210 dating and total As and Ni concentrations measured by Cornett and Chant (1986).

d) Calculate the rates of Ni and As diffusion from sediments to water using porewater profiles measured by Cornett and Chant (1986), and diffusion coefficients and the boundary layer thickness estimated from published values.

e) Evaluate the significance of remobilization/back diffusion of Ni and As from bottom sediments into the overlying water.

1.3 BACKGROUND

After the discovery of gold in the Moira River Basin (Figure 1) about 1860, numerous mining, milling, smelting and tailings operations introduced a diversity of heavy metals into the Moira River (Mudroch and Capobianco 1980). Several of these ores contained Ni and As (Bowles 1982).

The history of ore processing operations is not known quantitatively. The stratigraphy of metal concentrations in the bottom sediments suggests Ni and As have discharged into the lake throughout the past century (Evans et al. 1986; Cornett and Chant 1986). However operations ceased in 1961 and records suggest that the amount of arsenic flowing into Moira Lake through the Moira River has decreased (Ontario Ministry of the Environment, unpublished data). Inputs of Ni and As have been further reduced by a water purification plant that treats groundwater leachate flowing from the tailings. Large historical variations of Ni and As inputs and the large easily exchangeable fractions of these elements present in the bottom sediments (method of Tessier et al. 1979), suggests that the bottom sediment lake-water system of Moira Lake may not be at a steady state. As a result significant back diffusion may occur. Measurable levels of Ni and As in all compartments in Moira Lake provide a useful study system in which to estimate the fluxes of the elements between water and sediments.

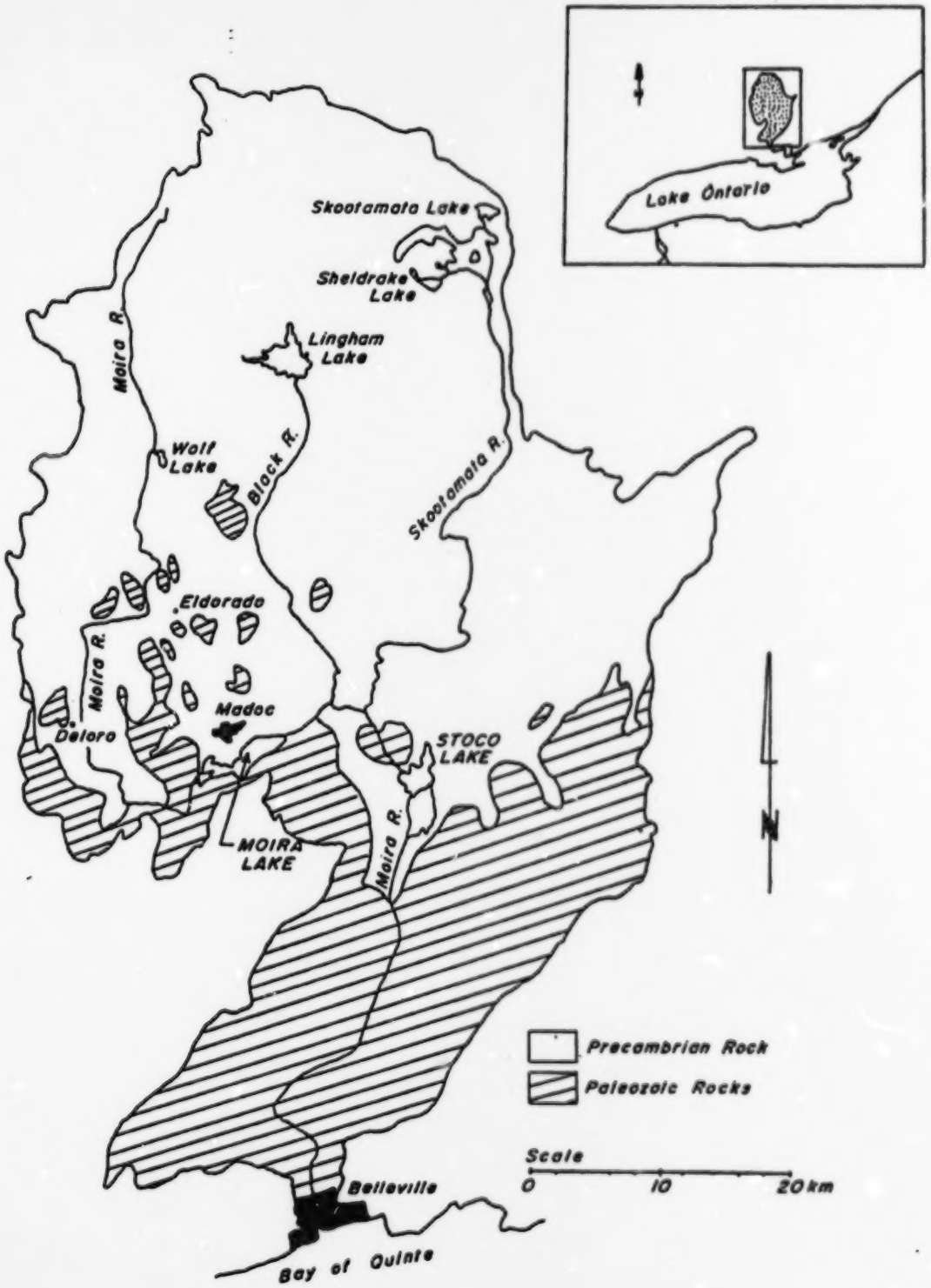


Figure 1 - MOIRA RIVER WATERSHED
(Source : Mudroch & Capobianco 1980)

2.0 METHODS

2.1 STUDY SITE

Moira Lake, located near Tweed, Ontario (latitude 44°30'N, longitude 77°27'W; Figure 1) is a large (827 ha) eutrophic lake formed by a widening in the Moira River (Mudroch and Capobianco 1980). Its mean depth is 4.4 m. The bedrock of the area was described by Sibul et al. (1974), as consisting of Precambrian rock of plutonic origin exposed in the northern part of the basin, but overlain by up to 83 m of limestone in the southern areas. The lake water pH is ≈ 8.0 and the alkalinity and hardness > 125 ppm suggest that the lake is buffered by the carbonates in the catchment. Moira Lake has two basins separated by a narrow constriction about 2 m deep with the major inflow containing the nickel and arsenic entering the smaller, shallower basin at the head of the lake. This inflow, the Moira River, supplies the majority of the water to Moira Lake. The lake flushes approximately 2.9 times per year (Evans et al. 1986).

2.2 SAMPLING METHODS

Water samples and cores of lake bottom sediment were collected on November 14, 1985. The location of the sampling sites is shown in Figure 2. All cores were collected with a K-B gravity corer using 7.0 cm inner diameter lucite core tubes. The water overlying the cores was removed and the cores were sectioned in 1 cm or 2 cm sections under a nitrogen atmosphere. As an additional precaution, the outer ring of core material (0-5 cm) was removed and stored, but was not used for any redox sensitive analyses. Then all samples were frozen in containers purged with nitrogen gas to prevent oxidation of the samples.

Triplicate water samples (1 L) were collected by pumping water at station 1 from about 1 m above the sediments at a depth of ≈ 7.0 m, using a peristaltic pump and Tygon[C] tubing into precleaned (soaking in HNO_3 24 hr) Nalgene[C] polyethylene bottles. The bottles were acidified with 1 mL of double distilled nitric acid and sealed in double plastic bags. Subsequent filtration and subsampling were performed in a clean room using a laminar flow hood.

2.3 ANALYTIC METHODS

Nickel and arsenic concentrations were measured in the dissolved (< 0.40 μm) and particulate fractions of Moira Lake water. Concentrations were also measured in the porewaters centrifuged (under nitrogen) from sectioned (2 cm intervals) sediment cores and in acidic extracts from the cores. The Ni and As in each sediment core section were extracted sequentially by the procedure of Tessier et al. using the modifications described in Cornett and Chant (1986). The total values used in this report are the sum of the concentrations of all extracts. Ni concentrations were measured by atomic absorption spectroscopy using graphite furnaces and a Zeeman background correction (Vollkopf et al. 1983). Arsenic concentrations were measured using hydride generation atomic absorption spectroscopy (Peacock and Singh 1981). Additional details are given in Cornett and Chant (1986).

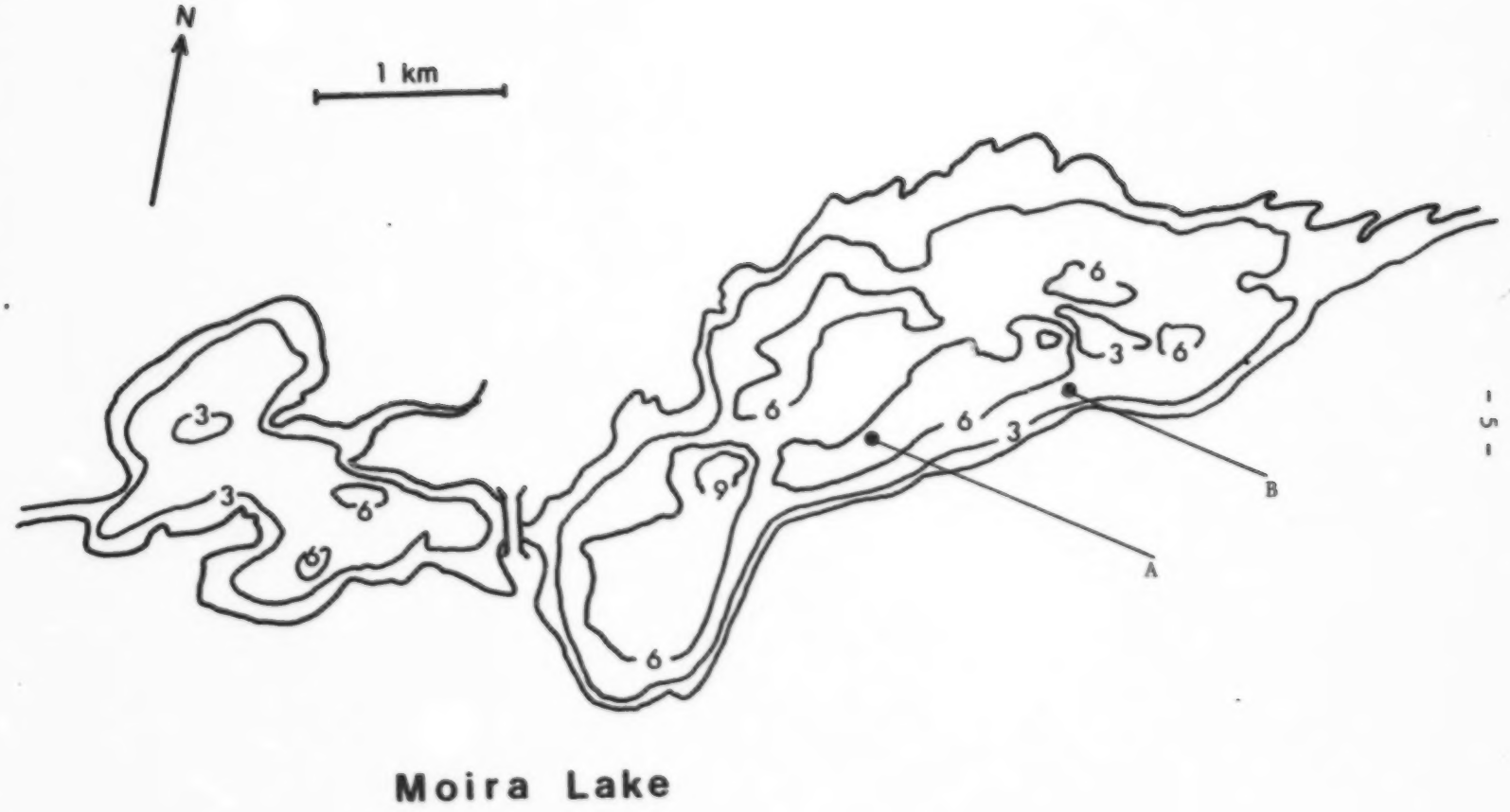


FIGURE 2. Lake morphometry and location of sediment cores collected in 1985 (●).

For Pb-210 analyses, core sections were dried to constant mass and homogenized using a shatter box. Often there was insufficient material from the inner section of a slice remaining for analyses at depths between 0 and 10 cm. Therefore the outer 0.5 cm section of the core was used for Pb-210 analyses of these sections. The larger dry mass of sections collected below 10 cm provided sufficient material for analyses.

The concentration of Pb-210 was determined assuming secular equilibrium between Pb-210 and its daughter Po-210. The activity of Po-210 was measured using alpha spectrometry. The extraction and plating technique of Eakins and Morrison (1977) was modified slightly. To obtain acceptable recoveries of the Po-209 yield tracer (mean recovery 75%), the Po was volatilized from the sediments at ≈650 to 700°C. The vapours were condensed, the condensors were then digested for four hours with concentrated nitric acid. Following removal of the nitric acid by evaporation, Po-210 was spontaneously electroplated on silver discs over a period of 16 to 24 hours. The discs were counted using surface barrier detectors, and the counts accumulated in a multichannel analyzer.

2.4 QUALITY ASSURANCE

Details of the quality assurance procedures used during the analyses of Ni and As are given in Cornett and Chant (1986). For the Pb-210 analyses, three procedures were used to insure their accuracy and precision.

1) We used a radiochemical yield tracer (Po-209) traceable to NBS SRM 4327, and confirmed the yield tracer activity against Pb-210/Po-210 solutions from Amersham Nuclear, and other laboratories.

2) We measured the activity of CANMET Energy Mines and Resources SRM DL-1A and our results agree with the expected value (Table 1).

3) Blanks analyzed by our procedures show no detectable activity above counter background. Counter background of the counting system was monitored at approximately biweekly intervals and was found to be < 1% in all but the lowest activity samples.

TABLE 1

SUMMARY OF Pb-210 QUALITY ASSURANCE TESTS

MATERIAL	EXPECTED ACTIVITY ($Bq \cdot g^{-1}$)	MEASURED ACTIVITY ($Bq \cdot g^{-1}$)
Po-209 yield tracer	5.24 ±0.15	5.23 ±0.78*
EMR SRM DL-1A	1.40 ±0.03	1.33 ±0.16

* also confirmed with Dr. G. Brunskill, Freshwater Institute, Winnipeg, Manitoba

3.0 RESULTS

3.1 Pb-210 DATING CORES

Pb-210 concentrations and depth profiles measured at sites A and B (Figures 3 and 4, Appendix 1) are similar to those reported in other studies (e.g. Robbins and Edgington 1975; Evans and Rigler 1983). Depth is expressed as cumulative dry mass to avoid the problems caused by compaction of the sediment through time (Robbins 1978). The most significant trends are:

1) Mixed layers of constant Pb-210 concentrations in the top 5 cm at site A and 7 cm at site B.

2) The exponential decrease in Pb-210 concentration below the mixed layer to levels supported by Ra-226 which are about 100x lower than surficial sediment concentrations.

3) The change in Pb-210 concentrations at site B occur rapidly from depths of 8-14 cm compared to the much slower exponential decrease occurring between 6-26 cm at site A.

We used the constant rate of supply model of sediment accumulation (Robbins 1978; Appleby and Oldfield 1978) to interpret the Pb-210 profiles, calculate rates of sediment accumulation and date the core stratigraphy. Below the mixed layer, the concentration of Pb-210 (C_w) at depth w is described by:

(1) $$C_w = C_o\, e^{-kw} + C$$

where: C_w is the concentration of Pb-210 measured in $Bq \cdot g^{-1}$ dry wt, w is the depth measured as g dry mass per cm^2, C_o is the surface concentration of Pb-210, and C is the concentration of supported Pb-210 in the sediments. The slope of the regression of $\ln(C_w - C)$ on w gives the constant (k) of decrease of unsupported Pb-210 with depth expressed as $g^{-1} \cdot cm^2$, and the sediment accumulation rate (r) in $g \cdot cm^{-2} \cdot yr^{-1}$ is given by:

(2) $$r = \lambda / k$$

where λ is the decay constant of Pb-210 ($0.03114 \cdot yr^{-1}$). The Pb-210 concentrations supported by Ra-226 (C) used in the calculation were 0.085 and 0.0091 $Bg \cdot g^{-1}$ for sites A and B respectively. These concentrations were measured in the deepest sections of the cores and values of k are insensitive to the value of C selected.

The Pb-210 concentrations used to calculate k values are shown in Appendix 1. From those regressions average rates of sediment accumulation (Table 2) were 149±20 and 101±33 g dry weight $\cdot m^{-2} \cdot yr^{-1}$ at sites A and B respectively. The accumulation rates are more similar than those judged from the concentration-depth profiles (Figures 3 and 4) because the density of sediment was lower at site A than at site B, and the depth scale differs on the graphs. However the composition of sediment at site B changes with depth from organic gyttja to inorganic sand and shells below 10 cm (Cornett and Chant 1986) and the bottom of the core appears to be an area of old river/lake shore. These

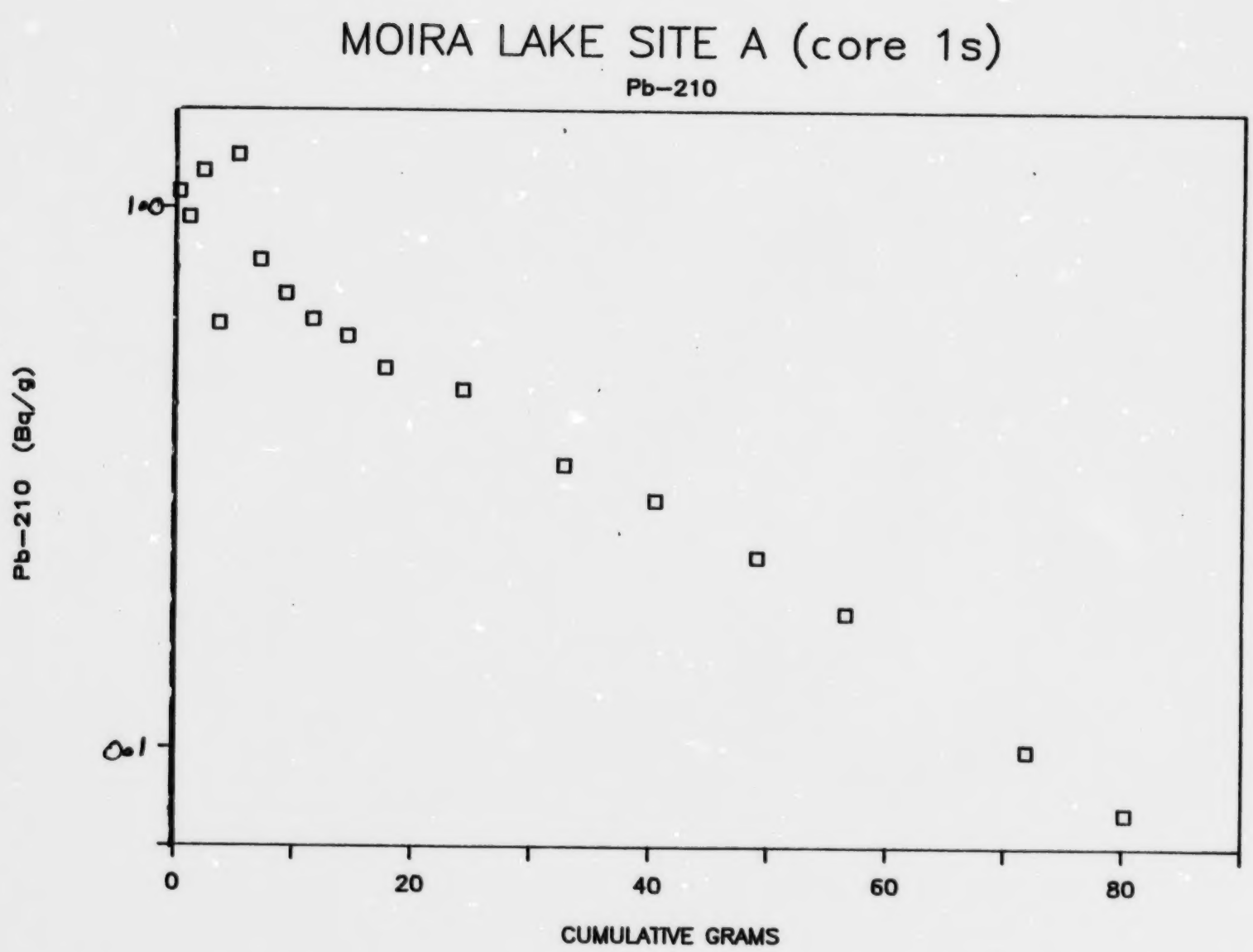

MOIRA LAKE SITE A (core 1s)
Pb-210
Pb-210 (Bq/g)
1.0
0.1
0
20
40
60
80
CUMULATIVE GRAMS

FIGURE 3

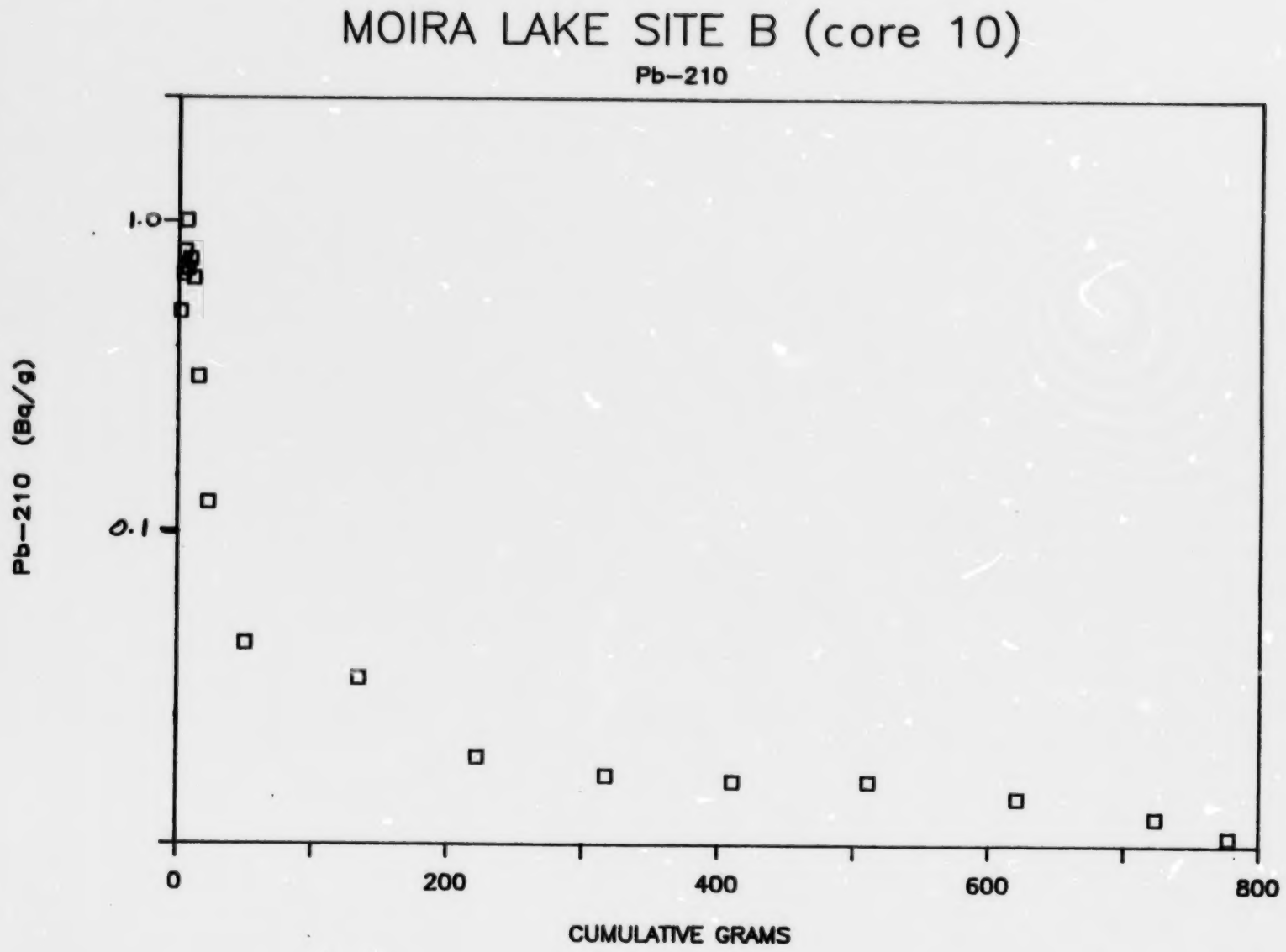

MOIRA LAKE SITE B (core 10)
Pb-210
1.0
0.1
Pb-210 (Bq/g)
0
200
400
600
800
CUMULATIVE GRAMS

FIGURE 4

variations in composition and bulk density complicate the interpretation of the changes in Pb-210 concentration because very old inorganic sediment appears to be mixed with recently deposited gyttja. Since this could bias the age determinations, the strata ages in core B must be interpreted with caution.

3.2 Ni AND As ACCUMULATION IN SEDIMENTS

Using the Pb-210 stratigraphy, the sediment accumulation rates reported in Section 3.1 and the total Ni and As concentrations measured by Cornett and Chant (1986), the history of Ni and As inputs in the sediments and the rates of Ni and As accumulation can be determined. In the surficial sections of cores from both sites, the sediments are mixed so that the detailed stratigraphy cannot be interpreted. We calculate the mixed layer ages from the dry mass of sediment of constant Pb-210 activity divided by r, the sediment accumulation rate. Depths included in the mixed layers were 0-5 cm and 0-7 cm at sites A and B representing 11 and 27 years respectively. The chronology of Ni and As concentrations below the mixed layer is shown in Figure 5. From these measurements the maximum inputs of Ni and As occurred approximately 40 years ago and were ≈ 5-10 times greater than inputs into the mixed layer.

The rates of Ni and As accumulation in the sediments at sites A and B can be calculated as the product of the dry mass accumulation rate multiplied by the concentration of Ni or As in the sediment. Ni and As concentrations in the sediments could be calculated from two different measures. Arsenic and nickel concentrations on particles in the water were less than the average concentrations measured in the mixed layer (Table 3). We interpret these differences as indicative of recent decreases in arsenic and nickel inflows to Moira Lake. However only a fraction of the Ni (2.1%) and As (4.0%) was bound to seston in the water and these seston measures were made on only one date. Since there are significant seasonal changes in arsenic concentration in the lake water (Ontario Ministry of the Environment, unpublished data) and probably similar changes in Ni concentration, we do not have sufficient data to resolve the trend in recent Ni or As inputs to Moira Lake. A more detailed mass balance study is needed to determine the fraction of Ni and As input to the lake that is retained in the sediments. The small fraction of Ni and As bound to particles suggest that retention is a small fraction of the input.

Accumulation rates of Ni and As were calculated using both estimates of element concentration (Table 4). The estimates range from 9 to 112 mg arsenic $m^{-2} \cdot yr^{-1}$ and 1.3 to 64 mg Ni $\cdot m^{-2} \cdot yr^{-1}$ at sites A and B. Higher accumulation rates of As than Ni in the sediments may reflect higher inputs of As than Ni during recent years. These rates of trace element accumulation are very high compared to those reported at other sites (e.g. Nriagu 1983; Carignan and Nriagu 1985).

3.3 Ni AND As DIFFUSION IN POREWATER

The inputs of Ni and As into Moira Lake water and into the bottom sediments have changed significantly over the past 100 years. As a result there is a large reservoir of both elements in the sediments that may not be in a steady state with concentrations in the water. Significant differences in Ni and As concentrations between bottom sediments and overlying water exist on

TABLE 2

SEDIMENT ACCUMULATION RATES DETERMINED BY Pb-210 DATING

Site	Rate ($g \cdot m^{-2} \cdot yr^{-1}$)	±1 SD	N
A	149	20	6
B	101	33	4

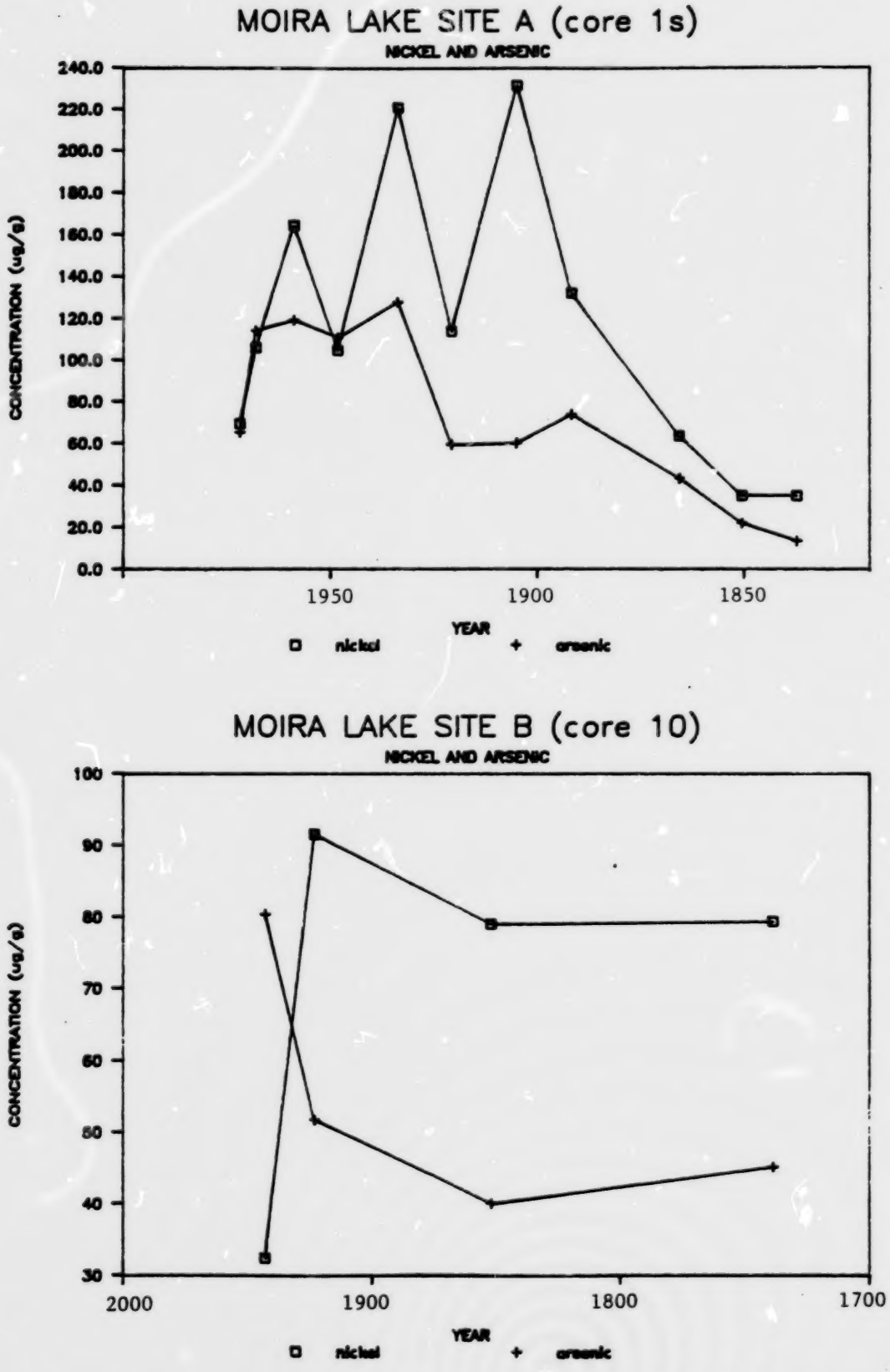


FIGURE 5. Chronology of As and Ni sediment concentrations.

TABLE 3

NI AND AS CONCENTRATIONS ON PARTICLES
CALCULATED FROM CORNETT AND CHANT (1986)
VALUES ARE EXPRESSED PER GRAM DRY WT.

	As ($ug \cdot g^{-1}$)	Ni ($ug \cdot g^{-1}$)
Seston	93 ±13	13 ±8.6
Site A: mixed layer (0-5 cm)	756 ±266	430 ±152
Site B: mixed layer (0-7 cm)	325 ±115	143 ±60

TABLE 4

RECENT ACCUMULATION RATES OF Ni AND As
IN THE BOTTOM SEDIMENTS OF MOIRA LAKE

		As ($mg \cdot m^{-2} yr^{-1}$)	Ni ($mg \cdot m^{-2} yr^{-1}$)
Site A:	Instantaneous (1986)*	14	1.9
Site A:	Mixed layer (1975-1986)	112	64
Site B:	Instantaneous (1986)*	9.3	1.3
	Mixed layer (1959-1986)	33	14

* based on measured particle concentrations

particles and in the dissolved phase (Cornett and Chant 1986). These concentration gradients permit transport of Ni and As down the concentration gradients from the sediments to the water on resuspended particles and by diffusion in the porewater and across the mud-water interface. To evaluate the significance of diffusion we have calculated the diffusive fluxes of Ni and As using Fick's first law,

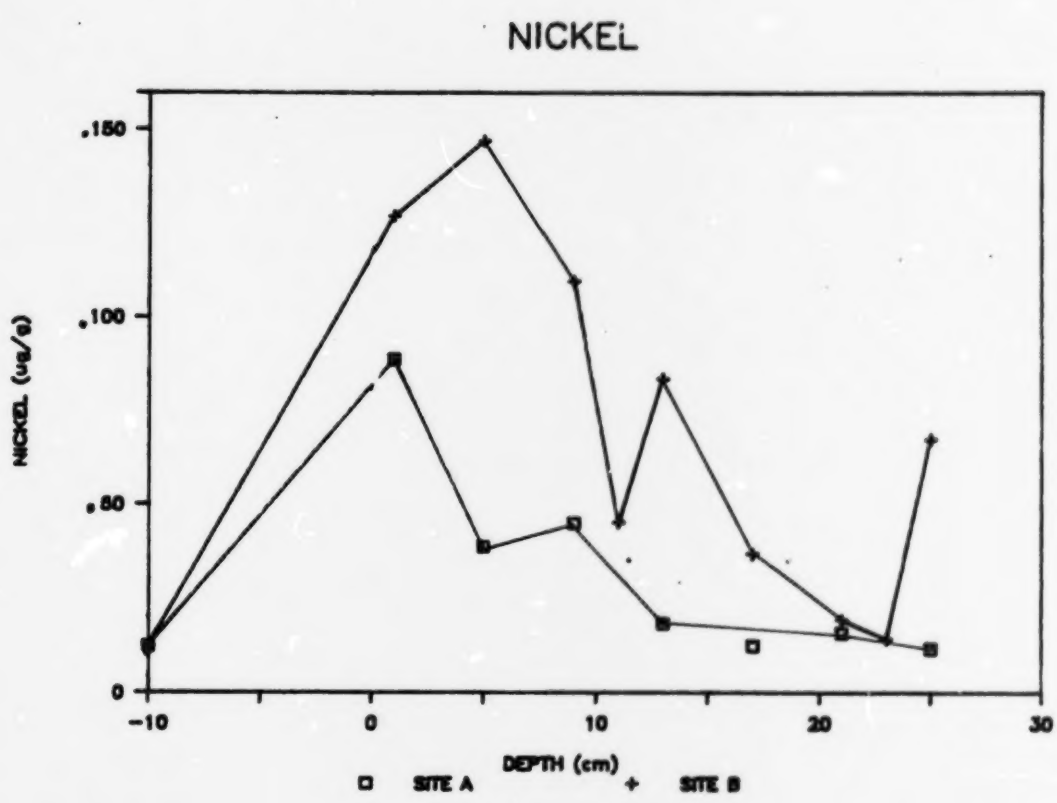
$$(3) \qquad F = -\phi D_c \frac{dc}{dz}$$

ϕ is the porosity of the sediments, where F is the diffusive flux of the element ($mg \cdot m^{-2} \cdot yr^{-1}$), D_c is the diffusion coefficient for the substance ($m^2 \cdot yr^{-1}$) and dc/dz is the depth-concentration gradient ($mg \cdot m^{-3} \cdot m^{-1}$) measured at the boundary between the water and the sediments. The sign convention used in (3) defines downward fluxes to be positive while upward fluxes are negative (i.e. loss from the sediments). Methods of estimating each of the variables in (3) are described below.

The water content of the surficial sediments is very high at sites A and B (> 90%; Cornett and Chant 1986; see Appendix 2). Therefore we have assumed ϕ=1 and tortuosity effects are negligible (Li and Gregory 1974). Ideally the diffusion coefficient of each chemical species should be measured under in situ conditions and must include any random transport mechanism such as biological or physical mixing, convective mixing, gas ebullition, etc. We have not measured D_c. Instead we approximate D_c by the molecular self diffusion coefficient calculated at the in situ temperature by the Stokes-Einstein relation (Li and Gregory 1974). Several studies support the contention that diffusion in the sediments occurs at molecular rates and is only slightly enhanced by the mixing processes occurring in lakes (Hesslein 1980; Bergman 1984; Carignan and Nriagu 1985). The water and surficial sediment temperatures were identical (2±0.2°C) at the time the cores and water samples were collected. Therefore we used this temperature for estimates of the instantaneous diffusion coefficients at that time and the annual average lake temperature (6°C) for long term average calculations.

The self diffusion coefficient for any ion also depends upon the charge and size of the ion. Based upon the Eh, pH and ionic strength of the pore water, we believe that the dominant ions present near or at the sediment-water interface are Ni^{2+} (Carignan and Nriagu 1985) and $H_2AsO_4^{2+}$ (Ferguson and Gavis 1972). The coefficients of molecular diffusion for these dominant species are 6.8×10^{-6} $cm^2 \cdot sec^{-1}$ and 9.05 $cm^2 \cdot sec^{-1}$ at 25°C. These coefficients, corrected to in situ temperatures were used in all calculations.

The final term required to estimate the diffusive fluxes are the concentration gradients of Ni and As. The gradients are scale dependent since they depend upon the distance between two or more concentration measurements. Dissolved Ni and As concentrations were measured by Cornett and Chant (1986) at 2 cm intervals within the porewater and ~ 1.0 m above the mud-water interface. We used these pore water concentrations measured at 2 cm intervals to calculate the difference in concentration in the pore water. To estimate the concentration gradient at the interface we have extrapolated concentrations measured in the pore water to the mud-water interface using a regression and assumed the concentration above the boundary layer at the mud-water interface is



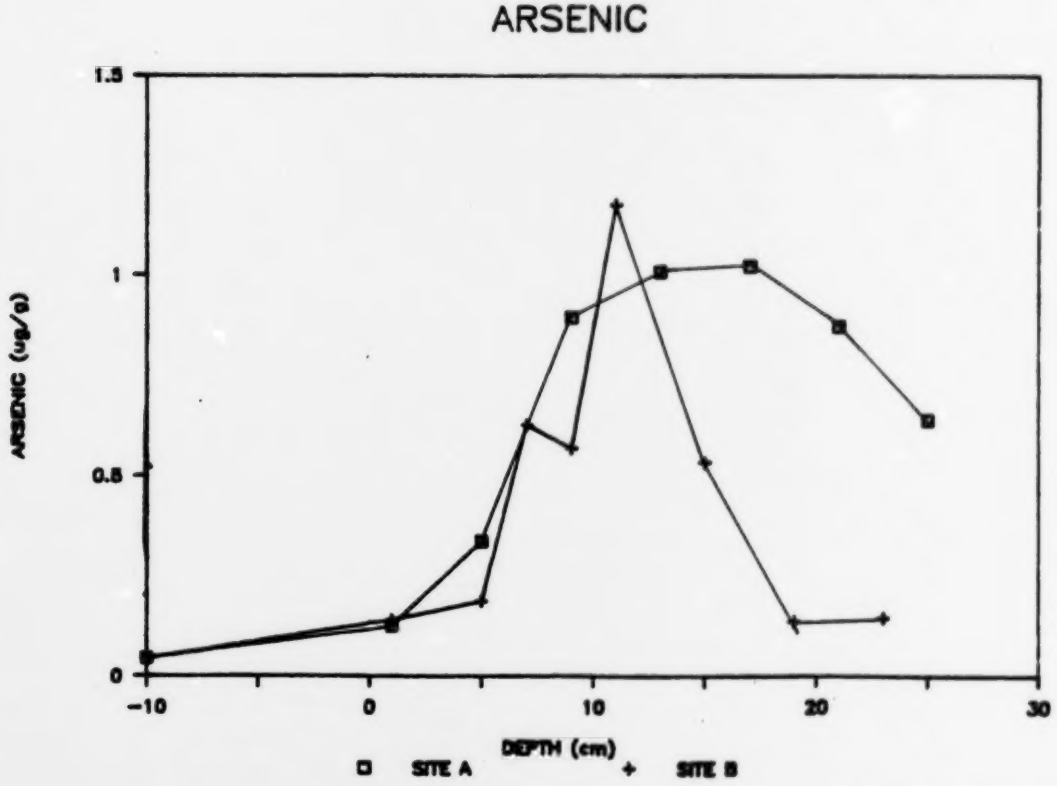


FIGURE 6. Ni and As concentrations in sediment porewaters.

equivalent to that measured 1.0 m above the sediments. This approximation is reasonable since the lake was mixed vigorously at the time of sampling (Cornett and Chant 1986). The length of thickness of the diffusive boundary layer at the mud-water interface was estimated to be 1000 μm based upon the experiments of Santschi et al. (1983).

The porewater and lake water concentrations summarized in Figure 6 demonstrate the complex nature of diffusive transport in the lake sediments. Arsenic is transported from the region of high concentrations, 10-15 cm below the mud-water interface deeper into the sediments and it is also migrating towards the interface and across the mud-water interface into the water column (Table 5). Ni also is diffusing both up and down the sediment column (Table 6). These Ni profiles suggest very intense mobilization/desorption at/near the interface since Ni is simultaneously diffusing in both directions and the gradients of dissolved Ni concentration change direction near the mud-water interface (Figure 6). This suggests the diffusive fluxes near the interface must be interpreted very cautiously until direct estimates of the concentration gradients on a very fine depth scale are made.

Calculated average and instantaneous rates of Ni and As diffusive transport are larger than the current rates of Ni and As accumulation in the sediments (Table 4). The rates are similar to the maximum rates of Ni and As accumulation ≈ 40 years ago. We interpret these calculations to support the hypothesis that back-diffusive remobilization from sediments to water is a significant transport process. It is difficult to compare rigorously the diffusion rates with the accumulation of Ni and As calculated from Pb-210 dating of the cores. Core dating provides average measures over multiyear periods. We do not have sufficient estimates of the Ni and As concentration gradients and their temporal variability to extrapolate confidently over the same period of years. Temperatures, biological activity and redox conditions all vary seasonally and may indirectly alter the concentration gradients and rates of diffusion. However at the time these measurements were made in November 1986, calculated diffusive transport across the oxic mud-water interface was rapid providing a significant input of both elements to the overlying water in Moira Lake. The flux calculations also are consistent with rapid transport of Ni and As within the sediment pore waters. Arsenic concentrations in the pore waters parallel total arsenic concentrations on the matrix (Cornett and Chant 1986) suggesting the larger inputs of As ≈ 40 years earlier are diffusing down concentration gradients within the sediments. Nickel concentrations in the pore waters do not mimic the depth profile of total Ni in the sediments. Nickel concentrations in pore waters near the mud-water interface are higher than concentrations measured deeper in the cores. Nickel appears to diffuse deeper into the sediments where it is precipitated as NiS (Millerite) under the reducing conditions that are present below approximately 6 cm.

TABLE 5

ARSENIC CONCENTRATION GRADIENTS (dc/dz) AND DIFFUSIVE FLUXES WITHIN THE PORE WATERS AT SITES A AND B*

	Site A			Site B		
Depth Interval (cm)	dc/dz ($g \cdot m^{-4}$)	Flux ($mg \cdot m^{-2} \cdot a^{-1}$)	Annual Flux ($mg \cdot m^{-2} \cdot a^{-1}$)	dc/dz ($g \cdot m^{-4}$)	Flux ($mg \cdot m^{-2} \cdot a^{-1}$)	Annual Flux ($mg \cdot m^{-2} \cdot a^{-1}$)
BL**	-55.	-770	-890	-30.	-420	-480
0-1	-4.0	- 56	- 65	-50	- 70	- 81
1-5	-1.2	- 16	- 19	-120	- 75	- 86
5-7	-22.	-310	-360	-	-	-
7-9	-3.0	- 41	- 47	-	-	-
9-11	+30.	-430	-460	-115	+ 79	+ 92

* transport deeper into the sediments is defined as positive
** BL = boundary layer

TABLE 6

NICKEL CONCENTRATION GRADIENTS (dc/dz) AND DIFFUSIVE FLUXES WITHIN THE PORE WATERS AT SITES A AND B*

	Site A			Site B		
Depth Interval (cm)	dc/dz ($g \cdot m^{-4}$)	Flux ($mg \cdot m^{-2} \cdot -1$)	Annual Flux ($mg \cdot m^{-2} \cdot a^{-1}$)	dc/dz ($g \cdot m^{-4}$)	Flux ($mg \cdot m^{-2} \cdot a^{-1}$)	Annual Flux ($mg \cdot m^{-2} \cdot a^{-1}$)
BL	-62	-660	-760	-62.	-660	-760
0-1	-52	- 55	- 63	-14	- 15	- 17
1-5	+60	+5.0	+6.1	+60	+ 13	+ 15
5-7	-	-	-	-	-	-
7-9	-	-	-	-	-	-
9-11	+56	+ 34	+ 39	+27	+7.1	+8.2

* transport deeper into the sediments is defined as positive

4.0 DISCUSSION

Relatively large amounts of Ni and As have accumulated in the bottom sediments of Moira Lake during the past 150 years. The transport of both elements across the sediment-water interface is controlled by the accumulation rate of particle bound Ni or As sorbed to settling particles and by the diffusion of the elements along concentration gradients across the mud-water interface. The magnitude and direction of these two processes determine the long term fate of contaminants input into freshwaters.

Bulk sediment accumulation rates in Moira Lake (100-150 $g \cdot m^{-2} \cdot yr^{-1}$) are similar to those measured in other mesotrophic/oligotrophic Canadian lakes (e.g. Evans and Rigler 1980; Robbins 1980; Evans et al. 1986). Higher rates of bulk sediment accumulation correlate with higher rates of Ni and As accumulation measured at the two sites in this study and at other sites in Moira Lake (Evans et al. 1986). The correlation between bulk sediment accumulation rate and elemental accumulation appears to be valid in a diversity of lakes for many elements.

The diffusive fluxes of As and Ni were calculated from the product of the diffusion coefficient multiplied by the element's concentration-depth gradient in the sediment pore water. The concentration gradients of both As and Ni were complex. Transport of As occurs both up and down the sediment column away from the highest concentrations of As deposited more than 40 years ago. Profiles of Ni concentration indicate that it is transported from the mud-water interface deeper into the sediment column. This concentration gradient is maintained by the continual precipitation of NiS deeper in the reducing zones of the sediments. Similar behaviour of Ni and other elements within reducing sediments has been reported in acidic lakes near Sudbury, Ontario (Carignan and Nriagu 1985). However the interpretation of Ni transport is complicated by the significant opposite gradient in dissolved Ni concentration at or above the mud-water interface. Ni concentrations in the overlying water are significantly lower than those in the surficial pore water. Explanations for the complex Ni concentration profiles include:

1) There is rapid mineralization/desorption at the interface allowing Ni to simultaneously diffuse both into the water and deeper into the sediments.

2) Methodologies for measurements of dissolved Ni in the lake water and pore water are not identical and the results cannot be compared.

3) The depth interval between the measures ($\geq$ 0.02 m) was not sufficiently small to provide a correct interpretation of the measures.

Since similar Ni concentration profiles were reported by Carignan and Nriagu (1985) in McFarlane Lake using different methods, explanations 2 and 3 seem unlikely to alter conclusions about the direction of the concentration gradient. It is unlikely that these Ni profiles are representative of steady state conditions. The lake was mixing vigorously during the sampling period and changes in redox conditions at the sediment interface frequently accompany

mixing events (Berner 1980). Further sampling is needed to evaluate the observed Ni profiles.

The rates of Ni and As diffusion within the porewater are significant. At all depths diffusive transport is more rapid than the recent accumulation rates of Ni and As calculated by Pb-210 dating. This observation cannot be correct over long periods of time because no Ni or As would accumulate in the sediments. Explanations for the very high diffusive fluxes include:

1) Recent redox changes have altered concentration gradients so that the measured values are not indicative of annual average values.

2) The calculated diffusion coefficients were overestimated substantially.

Carignan and Nriagu (1985) also calculated Ni fluxes into the sediments to be higher than accumulation rates determined by Pb-210 dating. This dicotomy cannot be resolved without further measurements. We can conclude that our best estimates of the diffusive fluxes show there appears to be rapid remobilization or back diffusion of Ni and As across the mud-water interface. A more detailed study of this problem is required.

5.0 CONCLUSIONS AND RECOMMENDATIONS

1. Measurements of bulk sediment accumulation rates in Moira Lake are similar to those in other lakes.

2. Rates of Ni and As accumulation in the bottom sediments show maximum accumulation occurred ~ 40 years ago. Current rates are 5-10x lower but are still much higher than background values measured in other lakes.

3. Ni and As are diffusing simultaneously from the porewater into the overlying water and deeper into the cores.

4. Diffusive fluxes of Ni and As are greater than those calculated from the accumulation of Ni and As in the bulk sediments.

5. The cause of the discrepancy between the soluble diffusive and particulate bound fluxes are unclear.

6. Models of Ni or As transport cannot ignore the diffusive transport between water and sediments.

7. The long term fate of Ni and As in the sediments is unclear. A more detailed study of the temporal variation in Ni and As in the porewater is needed and the transport estimates made here should be checked with independent methods.

8. Kinetics of Ni and As exchange between the solid sediment matrix and the porewaters may control porewater Ni and As concentrations and warrant further study.

6.0 ACKNOWLEDGEMENTS

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APPENDIX 1

Pb-210 AND DRY WEIGHTS OF MOIRA LAKE CORES

SITE A

SECTION (CM)	DRY WEIGHT (GMS)	CUMULATIVE DRY WEIGHT TO MIDPOINT (GMS)	ACTIVITY OF PB210 (BQ/G)
0-1	0.57	0.29	1.067
1-2	1.16	1.15	0.962
2-3	1.16	2.31	1.161
3-4	1.60	3.69	0.624
4-5	1.57	5.28	1.239
5-6	2.12	7.12	0.807
6-7	2.22	9.29	0.705
7-8	2.32	11.56	0.635
8-9	3.52	14.48	0.594
9-10	2.81	17.65	0.522
10-11	2.90	20.50	N/A
11-12	4.56	24.23	0.478 *
12-13	4.40	28.71	N/A
13-14	3.64	32.73	0.353 *
14-15	3.25	36.18	N/A
15-16	5.25	40.43	0.306 *
16-17	4.34	45.22	N/A
17-18	3.42	49.10	0.243 *
18-19	3.96	52.79	N/A
19-20	3.56	56.55	0.193 *
20-21	3.59	60.13	N/A
21-22	3.62	63.73	N/A
22-23	4.16	67.72	N/A
23-24	4.34	71.87	0.110 *
24-25	4.57	76.33	N/A
25-26	3.19	80.21	0.085
26-27	4.11	83.86	N/A

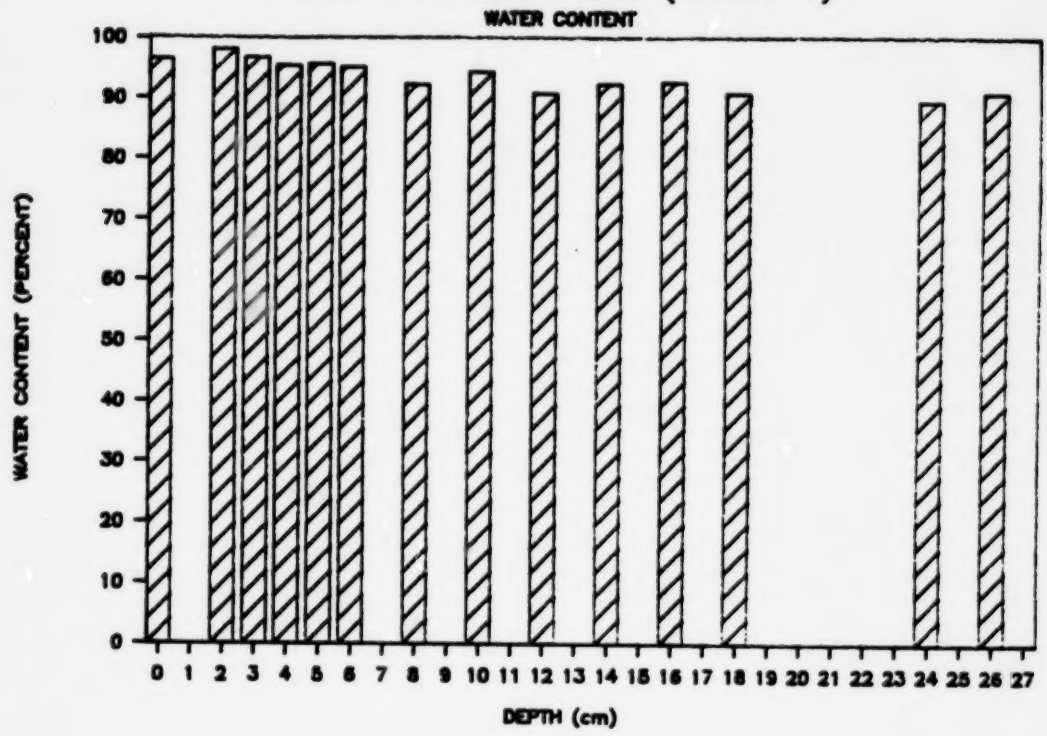
SITE B

SECTION (CM)	DRY WEIGHT (GMS)	CUMULATIVE DRY WEIGHT TO MIDPOINT (GMS)	ACTIVITY OF PB210 (BQ/G)
0-1	3.40	1.70	0.484
1-2	0.79	3.80	0.652
2-3	0.58	4.48	0.691
3-4	1.04	5.29	0.789
4-5	0.68	6.15	1.007
5-6	1.42	7.20	0.682
6-7	2.56	9.19	0.737
7-8	2.47	11.71	0.633 *
8-9	5.04	15.46	0.287 *
9-10	10.28	23.12	0.104 *
10-11	44.87	50.70	0.034 *
11-12	42.89	94.58	N/A
12-13	37.77	134.91	0.026
13-14	43.66	175.62	N/A
14-15	49.88	222.39	0.014
15-16	41.37	268.02	N/A
16-17	57.35	317.38	0.012
17-18	46.02	369.06	N/A
18-19	38.09	411.12	0.011
19-20	51.33	455.83	N/A
20-21	58.89	510.94	0.011
21-22	54.76	567.76	N/A
22-23	52.56	621.42	0.010
23-24	43.56	669.48	N/A
24-25	64.49	723.51	0.008
25-26	43.82	777.66	0.007

* data used to calculate C in equation 1.

APPENDIX 2

MOIRA LAKE SITE A (CORE 1)



MOIRA LAKE SITE B (CORE 10)